

# NOVEL APPROACHES FOR DETERMINATION OF DEGREE OF ASSOCIATION OF COAL-DERIVED PRODUCTS BY VAPOR PRESSURE OSMOMETRY

W.C. Lee, I. Schwager, T.F. Yen

University of Southern California, Chemical Engineering Department  
University Park, Los Angeles, California 90007

## INTRODUCTION

Vapor Pressure Osmometry (VPO) molecular weights of coal-derived asphaltenes obtained from coal liquids produced in five major coal liquefaction demonstration processes have been determined as a function of concentration in the solvents tetrahydrofuran (THF) and benzene (1). It was shown that association of coal-derived asphaltenes takes place in both solvents over the concentration range of 4-36g/l. In this study, the VPO molecular weights of the same asphaltenes have been obtained over a wider concentration range of 4-60g/l and a self-association model of asphaltenes in solution has been derived and the dissociation constants, one for the dissociation of dimeric complexes and one for the dissociation of higher order complexes, have been calculated with the aid of a modern computer.

This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution, although a number of other techniques have been used in the past (2-8, 13, 14).

## THEORETICAL

In order to investigate the self-association of phenol in carbon tetrachloride solution, Coggeshall and Saier (2) carried out an IR study of the hydroxyl stretching region of phenol and obtained very good agreement between theory and experiment by using two equilibrium constants. They derived the following two expressions:

$$\alpha_n = n\alpha \frac{K}{K_1} \left[ \frac{\alpha C}{K} \right]^{n-1} \quad 1)$$

$$K = \frac{C\alpha}{2(K_1 - K)} \left[ 2K_1 - \frac{\bar{K}}{2} + \sqrt{2K_1 \bar{K} + \frac{\bar{K}^2}{4}} \right] \quad 2)$$

where

- $n$  = integer
- $\alpha_n$  = fraction of monomer bound in nth polymer
- $\alpha$  = fraction of monomer unassociated
- $C$  = concentration in moles per liter
- $K_1$  = dissociation constant of dimer
- $K$  = dissociation constant of all other polymers  $=K_2=K_3\ldots$
- $\bar{K} = 2\alpha^2 C / (1 - \alpha)$

If  $C$  is the initial concentration of monomer before any association, at equilibrium the concentrations of monomer, dimer, trimer, etc., are  $C$ ,

$\frac{\alpha_2 C}{2}$ ,  $\frac{\alpha_3 C}{3}$ , ...,  $\frac{\alpha_n C}{n}$  and the molecular weights are  $M_0$ ,  $2M_0$ ,  $3M_0$ , ... and  $nM_0$ .

Since the molecular weight measured in VPO is the number average molecular weight, it is given that

$$MW_{obs} = \frac{Mo \alpha C + 2Mo \cdot \frac{\alpha_2 C}{2} + 3Mo \cdot \frac{\alpha_3 C}{3} + \dots + nMo \frac{\alpha_n C}{n}}{C \cdot \left[ \alpha + \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \dots + \frac{\alpha_n}{n} \right]} \quad 3)$$

where  $MW_{obs}$  is the number average molecular weight from VPO.

With the use of the relationship  $\sum \alpha_n = 1$ ,  $\frac{1}{1-x} = 1 + x + x^2 + \dots$ , and

Equation 1, one may simplify Equation 3 and get

$$MW_{obs} = \frac{Mo}{\alpha \left[ 1 + \frac{K}{K_1} \frac{1}{\frac{K}{\alpha C} - 1} \right]} \quad 4)$$

In theory, the equilibrium constants  $K$  and  $K_1$  can be obtained by solving Equations 2 and 4 simultaneously at two different concentrations. The approach will be discussed in the next section.

#### EXPERIMENTAL

Coal-derived asphaltenes were separated by solvent fractionation (9, 10) from coal liquids produced in five major demonstration liquefaction processes: Synthoil, HRI H-Coal, FMC-COED, Catalytic Inc. SRC, and PAMCO SRC.

A Mechrolab Model 301A Vapor Pressure Osmometer was used to determine molecular weights with benzil employed as a standard. Both the non-aqueous probe and the thermostat were designed for 37°C. In normal runs, 6-8 molecular weights over the range 4-60 g/l were measured in the solvents benzene or THF.

A modern computer was used to solve the calculation problem according to the following steps:

- Assume values of  $K$  and  $K_1$ .
- Calculate for  $\alpha$  and  $\beta$  at two concentrations,  $C_1$  and  $C_2$ , from Equation 4 where  $MW_{obs}$  is the molecular weight from VPO. When the concentration is  $C_1$ , the fraction of monomer unassociated at equilibrium is  $\alpha$ , and when the concentration is  $C_2$ , it is  $\beta$ .
- Substituting  $C_1$ ,  $C_2$ ,  $\alpha$  and  $\beta$  into Equation 2 and get

$$K = \frac{C_1 \alpha}{2(K_1 - \bar{K}_1)} \left[ 2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1 \bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right] \quad 5)$$

$$K = \frac{C_2 \beta}{2(K_1 - \bar{K}_2)} \left[ 2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1 \bar{K}_2 + \frac{\bar{K}_2^2}{4}} \right] \quad 6)$$

where  $\bar{K}_1 = 2 \alpha^2 C_1 / (1 - \alpha)$

$\bar{K}_2 = 2 \beta^2 C_2 / (1 - \beta)$

Since K is independent of concentration, by combining Equations 5 and 6, it is given that

$$\frac{\alpha C_1}{2(K_1 - \bar{K}_1)} \left[ 2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1\bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right] \\ = \frac{C_2\beta}{2(K_1 - \bar{K}_2)} \left[ 2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1\bar{K}_2 + \frac{\bar{K}_2^2}{4}} \right] \quad (7)$$

- (d) Solve Equation 7 for  $K_1$  by the Newton-Raphson method.
- (e) Calculate K from Equation 5 or 6.
- (f) Repeat the same procedures until the calculated values of K and  $K_1$  are close enough to the assumed values.
- (g) Using the equilibrium constants obtained above the molecular weights over the concentration range of 4-65 g/l can be calculated based on this model. The fraction of monomer unassociated at each concentration is obtained by solving Equation 2 and the fraction of monomer bound in any degree of polymer can be also obtained from Equation 1.

A number of different equilibrium constant pairs, K and  $K_1$ , have been tried for five asphaltenes in benzene. The ones which afford the minimum standard deviations between the experimental and calculated molecular weights have been chosen.

#### RESULTS AND DISCUSSION

The VPO molecular weights for all five coal-derived asphaltenes, in benzene are shown in Figs. 1 to 5. The results indicate that association of coal-derived asphaltenes takes place in both solvents over the concentration range of 4-60 g/l. The calculated equilibrium constants, together with the standard deviations are summarized in Table I where the % Dev. is defined as:

$$\frac{\text{Standard Deviation of MW}}{\text{MW of Monomer}} \times 100\%$$

All % Dev. values are less than 5.5%. This suggests that this two parameter model is efficient in describing the self-association of asphaltenes from five different processes in benzene and THF. The calculated molecular weights, fraction of monomer and monomer bound in dimer and trimer are also plotted in Figs. 1 to 5 for the five asphaltenes.

It is interesting to note from Equation 4 that  $MW_{obs} \approx Mo/\alpha$  as  $C \rightarrow 0$  and  $Mo/\alpha \approx Mo$  since  $\alpha \rightarrow 1$  as  $C \rightarrow 0$ . This agrees with the experimental results obtained from VPO and reported in Reference (1) that molecular weight values found in different solvents, by extrapolating the plots to infinite dilution are in accordance. These infinite dilution molecular weight values approximate the true monomer molecular weights and were used as  $Mo$  throughout this study.

The association of petroleum asphaltenes has been studied by a variety of techniques (3-8) and the mechanism of self-association has been described largely in terms of electronic association. The mechanism of bonding in coal-

derived asphaltenes is important and is under study (11). The association of these species has been reported in terms of hydrogen bonded complexes which can be separated into acidic and basic components (12). The hydrogen bonding of these two components and some model complexes has been further studied by NMR (13,14). Unfortunately, all of the reports on coal-derived asphaltenes contain only qualitative results. However, these studies tend to support the self-association model derived here, since it is very likely that in solution dimer could be formed through the bondings between the acidic proton and basic nitrogen or oxygen of two molecules or trimer could be formed through the bondings between those of three molecules. The association of monomer into dimer, trimer in solution depends on the solvent used. It is more significant in the less polar solvent benzene than THF, so the variation of molecular weights vs. concentration in benzene is greater.

This study is significant because, based on this model, the heat of formation of the polymers can be calculated from equilibrium constants at various temperatures and the mechanism of the bonding can be studied. This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution.

Comparing the equilibrium constants  $K_1$  and  $K$  of these five different asphaltenes in benzene, it is found that Synthoil and PAMCO SRC asphaltenes have stronger association between molecules while FMC-COED and Cat. Inc. SRC asphaltenes have less. The equilibrium constants in THF are generally larger than in benzene, since THF is more polar solvent and tends to dissociate the asphaltene molecules as they are dissolved. But this dissociation tends to go to completion in either solvent at infinite dilution.

The curves labeled 1,2,3 in Figs. 1 to 5 show the distribution of asphaltene between monomer, dimer and trimer as a function of total asphaltene concentration. For example, if 20 gm of Cat. Inc. SRC asphaltene is dissolved in 1 l benzene at 37°C, the fractions of monomer, dimer and trimer are 0.70, 0.18, 0.07 (from Fig. 1), while the remaining 0.05 is contained as polymers higher than trimer. The concentrations of monomer, dimer and trimer can be calculated and are:

$$\text{concentration of monomer (moles/l)} = \frac{20}{483} \times 0.7 = 2.9 \times 10^{-2} \text{M}$$

$$\text{concentration of dimer (moles/l)} = \frac{20}{483} \times 0.18 \times \frac{1}{2} = 3.7 \times 10^{-3} \text{M}$$

$$\text{concentration of trimer (moles/l)} = \frac{20}{483} \times 0.07 \times \frac{1}{3} = 9.7 \times 10^{-4} \text{M}$$

If the rest is assumed tetramer then concentration of tetramer (moles/l) =  $\frac{20}{483} \times 0.05 \times \frac{1}{4} = 5.2 \times 10^{-4} \text{M}$  where the number 483 is the molecular weight of monomer.

In benzene solution, as the concentration increases, the fraction of asphaltene existing as the dimer reaches a maximum, and then decreases, and higher multimers become increasingly important. In highly concentrated solutions these larger multimers start to precipitate. Evidence for association of monomeric asphaltenes into 4-6 average layers in the solid state has been found by x-ray diffraction spectroscopy (15).

- (1) I. Schwager, W.C. Lee, T.F. Yen, to be published, Anal. Chem., Vol. 49, Nov. 1977.
- (2) N.D. Coggeshall and E.L. Saier, J. Am. Chem. Soc., 73, 5414 (1951).
- (3) G.A. Sill and T.F. Yen, Fuel, 48, 61 (1969).
- (4) E.C. Tynan and T.F. Yen, Fuel, 48, 191 (1969).
- (5) T.F. Yen, E.C. Tynan, G.B. Vaughan, and L.J. Boucher, "Spectrometry of Fuels," (edited by R.A. Friedel) Plenum Press, N.Y. 1970, Chapter 14.
- (6) J.P. Dickie, M.N. Haller, and T.F. Yen, J. of Colloid and Interface Science, 29, 475 (1969).
- (7) J.P. Dickie and T.F. Yen, Anal. Chem., 39, 1847 (1967).
- (8) S.E. Moschopedis, J.F. Fryer and J.G. Speight, Fuel, 55, 227 (1976).
- (9) I. Schwager and T.F. Yen, Am. Chem. Soc., Div. Fuel Chem., Preprints, 21 (5), 199 (1976).
- (10) I. Schwager and T.F. Yen, in Liquid Fuels from Coal (R.T. Ellington, ed.), Academic Press, New York, N.Y., 1977, pp. 233-248.
- (11) T.F. Yen, in Workshop on Coal Chemistry Preprint, Stanford Research Institute, 1976, pp. 144-164.
- (12) H.N. Sternberg, R. Raymond and F.K. Schweighardt, Science, 188, 49 (1975).
- (13) F.K. Schweighardt, R.A. Friedel, and H.L. Retcofsky, Applied Spectroscopy, 30, 291 (1976).
- (14) S.R. Taylor, L.G. Galya, B.J. Brown, and N.C. Li, Spectroscopy Letters, 9, 733 (1976).
- (15) ERDA Report No. FE-2031-4, June 1976.

#### ACKNOWLEDGEMENT

This work was sponsored by U.S. DOE under contract no. E(49-18)2031, to whom the authors wish to express their appreciation.

Table 1. Calculated Equilibrium Constants and Standard Deviations of Coal-Derived Asphaltenes in Benzene

Process	Monomer MW **	$K_1$	$K_2$	Standard Deviation	% Dev.
Synthetic Asphaltene	560	0.0762	0.0671	13.7	2.4
IRI Asphaltene	492	0.118	0.0866	9.0	1.8
FMC-COD Asphaltene	375	0.210	0.0813	20.7	5.5
Cat. Inc. SRC * Asphaltene	483	0.225	0.109	12.2	2.5
PANCO SRC * Asphaltene	532	0.0610	0.0971	18.6	3.5

\* Isolated from vacuum distilled bottom product.

\*\* From Ref. (1).

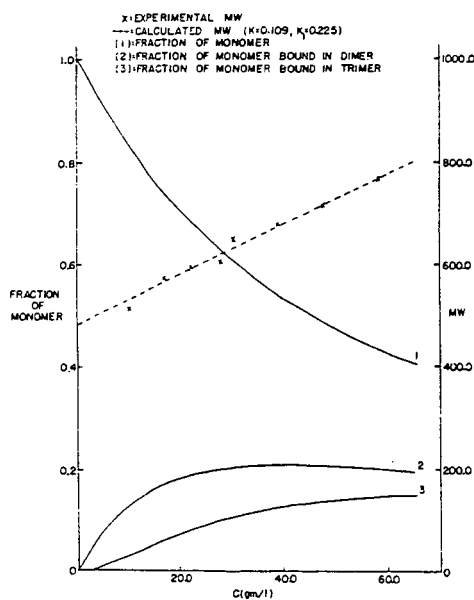


FIG. 1 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION CAT. INC. ASPHALTENE IN BENZENE

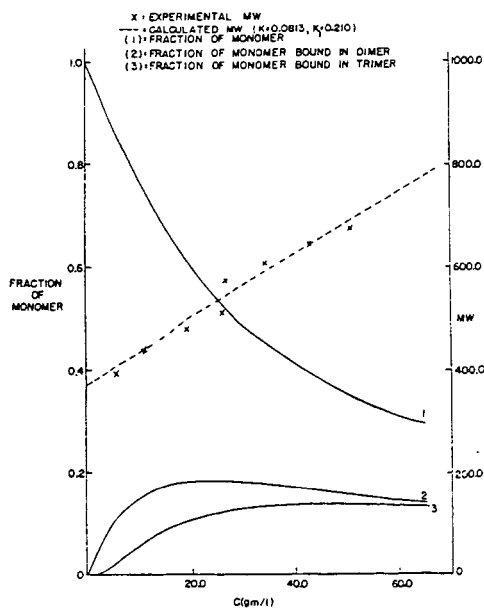


FIG. 2 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION FMC-COD ASPHALTENE IN BENZENE

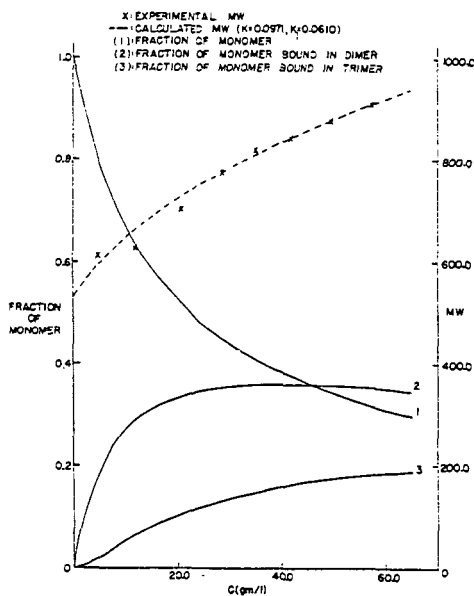


FIG. 3 FRACTIONS OF MONOMER AND VPC MW VS CONCENTRATION  
PAMCO ASPHALTENE IN BENZENE

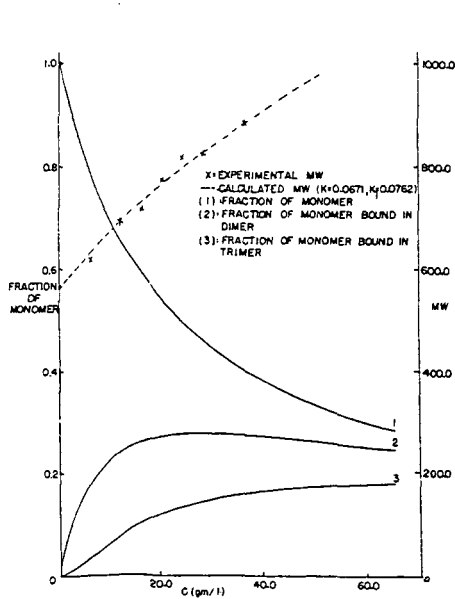


FIG. 4 FRACTIONS OF MONOMER AND VPC MW VS CONCENTRATION  
SYNTHOL ASPHALTENE IN BENZENE

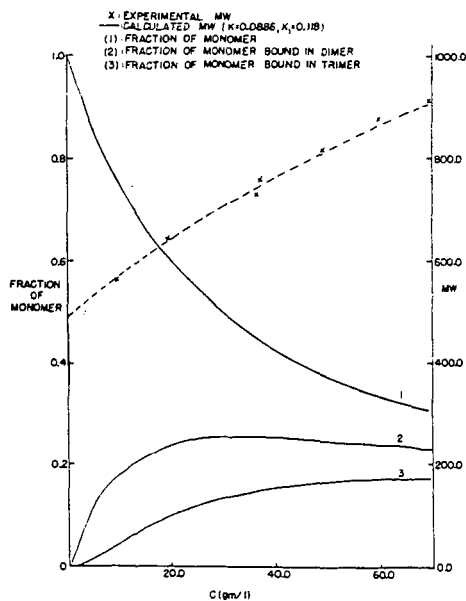


FIG. 5 FRACTIONS OF MONOMER AND VPC MW VS CONCENTRATION  
HRI ASPHALTENE IN BENZENE

## On the Distribution of Organic Sulfur Functional Groups in Coal.

Amir Attar and Francois Dupuis, Department of Chemical Engineering,  
University of Houston, Houston, Texas 77004.

### 1. SULFUR IN COAL

Traditionally, the sulfur in coal has been considered in two classes: 1) inorganic sulfur and 2) organic sulfur. In the class of inorganic sulfur, two types of compounds were considered: the disulfides and the sulfates. The organic sulfur is all the sulfur which is connected to the hydrocarbon matrix. Standard analytical techniques (1)(2)(3) are used to estimate the concentration of each class of sulfur in coal samples.

The inorganic sulfur, which is mainly iron pyrite,  $\text{FeS}_2$ , is present in the form of isolated crystals. Part of the  $\text{FeS}_2$  particles are usually separated from the coal by simple physical separation. However, the organic sulfur can be removed from coal only if the chemical bond between carbon and sulfur is broken. The chemistry, the thermodynamics and the kinetics of the reactions of sulfur in coal have been reviewed recently (4)(5)(6) and the reader is referred to these manuscripts for details.

The chemistry of the reactions of  $\text{FeS}_2$  and their rate are obviously different from that of the organic sulfur. Moreover, since the organic sulfur is present in the form of different functional groups, each functional group reacts at a different rate (6)(7).

### 2. ORGANIC SULFUR FUNCTIONAL GROUPS IN COAL

Very little data on the functional groups in which the organic sulfur appear and on their distribution has been derived by direct observation on coal. However, it is plausible to assume that the organic sulfur is present in coal in the same types of sulfur functional groups that can be found in oils and in other organic sulfur containing molecules. Moreover, if a general rule that applies throughout organic chemistry is applied to the sulfur in coal, we can say that the organic sulfur groups in coal react in the same way as their low molecular weight homologs and produce the same types of reaction products. For example, organic thiols,  $\text{RSH}$ , can be reduced by hydrogen to hydrogen sulfide,  $\text{H}_2\text{S}$ :



Thus, all the thiols, irrespective of the size and the shape of the radicals,  $\text{R}$ , can be reduced by  $\text{H}_2$  to  $\text{RH}$  and  $\text{H}_2\text{S}$ . Variations in the rate of the reduction may, however, exist for different  $\text{R}$ 's.

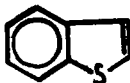
The most important sulfur functional groups in coal are believed to be:

1. derivatives of thiophenes and alkyl thiophenes

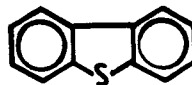
The most important parent structures are:



Thiophene



Thianaphene



Dibenzothiophene

2. aryl sulfides:  $\text{Ar-S-Ar'}$
3. aliphatic sulfides:  $\text{R-S-R}$
4. cyclo sulfides, e.g.,
5. thiaphenoles

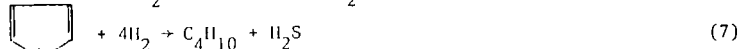
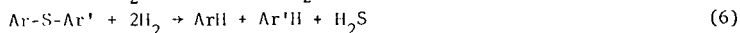
The presence of disulfides, sulfoxides, and sulfones were never demonstrated. It is believed that disulfides and sulfoxides are too unstable to survive the coalification process. Most of the organic sulfur is present in the forms of thiophenes and alkyl, aryl, and cyclic sulfides (4)(5)(6)(7). Most of the information was obtained from examination of the smaller molecular products



which were obtained by breaking the organic coal matrix (depolymerization). Obviously, the technique which is used to depolymerize the coal would have a deterministic effect on the results, since drastic depolymerization techniques may change the structures of the sulfur constituents as well as that of the hydrocarbon parts. Several reviews of the chemistry of sulfur in coal can be found in the older literature (8)(9)(10)(11)(12). Some aspects of the organic sulfur groups have recently been discussed by Attar and Corcoran (7).

### 3. THE PRINCIPLE OF THE PROPOSED METHOD OF ANALYSIS

All the sulfur groups in coal can be reduced by hydrogen to hydrogen sulfide,  $H_2S$ :



Each of these reactions has a given activation energy and a frequency factor which vary in a limited range for each group of sulfur compounds, when the structure of the organic radical is changed. Other reducing agents which contain hydrogen can be used with the same effective results:

These observations lead to the following important deductions: 1. If the activation energy  $E_{ai}$  and the frequency factor  $A_i$  for the rate of reduction of the  $i$ -th functional group are determined, the  $i$ -th group is uniquely characterized. In other words, a particular value of  $E_{ai}$  and  $A_i$  can belong only to the  $i$ -th group, and therefore they define the  $i$ -th group and 2. The exact amount of  $H_2S$  that evolves when the  $i$ -th group is reduced is proportional to the amount of the  $i$ -th sulfur group that has been reduced. If all the amount of the  $i$ -th group in the sample was reduced, then the amount of  $H_2S$  that evolved is proportional to the amount of the  $i$ -th group in the sample.

In order to be able to determine the total amount of each sulfur group in a fixed sample of coal, the following problems have to be solved:

1. How to determine the activation energy and the frequency factor for each sulfur group.
2. How to quantitatively reduce all the sulfur in a coal sample to  $H_2S$  and how to determine its amount.

The activation energies and the frequency factors can be determined using Juntgen method. Juntgen method and the methods which we proved that can be used to quantitize the  $H_2S$  are discussed in the next sections.

#### 3.1 JUNTGEN METHOD FOR THE DETERMINATION OF $E_{ai}$ AND $A_i$

Consider a sample which contains a fixed quantity of sulfur in the form of different functional groups. Let us assume that each group can be reduced to  $H_2S$  by a first order reaction. For example, consider the reduction of the aliphatic sulfides:



$$\frac{d[H_2S]_1}{dt} = k_1 [R-S-R'] \quad (9)$$

The index 1 was used to denote the sulfidic functional group;  $R-S-R'$ . Let's assume further that the rate constant,  $k_1$ , depends on the temperature according to Arrhenius equation:

$$k_1 = A_1 e^{-\frac{E_{a1}}{RT}} \quad (10)$$

where  $A_1$  is the frequency factor and  $E_{a1}$  the activation energy for the reduction. Then:

$$\frac{d[H_2S]_1}{dt} = A_1 e^{-\frac{E_{a1}}{RT}} [R-S-R'] \quad (11)$$

The rate constant of the reduction becomes larger at higher temperatures. That means that the rate of depletion of sulfide becomes larger at higher temperatures. The rate of evolution of  $H_2S$  from a sample with a fixed amount of the sulfide, which temperature is gradually increased, will increase initially due to the increase in the temperature, but since the concentration of the sulfur is depleted in the process, due to the evolution of  $H_2S$ , the rate will begin to decrease after most of the sulfur was reduced. The mathematical equation which describes the rate of evolution of gas as a function of the temperature of the sample, where the temperature is increased linearly with the time were developed by Juntgen (13)(14). Suppose that the temperature is increased according to:

$$T = T_0 + \alpha t \quad (12)$$

where  $T_0$  is the initial temperature ( $^{\circ}K$ ),  $\alpha$  the rate of heating,  $^{\circ}K/min$ , and  $t$  the time, min. Then the volume of  $H_2S$ ,  $V_i$ , that evolves when the  $i$ -th group is reduced, follows the equation:

$$\frac{dV_i}{dt} = \frac{A_i V_{i\infty}}{\alpha} \exp \left[ -\frac{E_i}{RT} + \frac{A_i RT^2}{E_i} \left( 1 - \frac{2RT}{E_i} \right) e^{-\frac{E_i}{RT}} \right] \quad (13)$$

where  $V_{i\infty}$  denotes the total volume of  $H_2S$  that will evolve as a result of the complete reduction of the  $i$ -th group. The graph of this function is sketched in Figure 1.

The temperature at which the rate of evolution of  $H_2S$  from the  $i$ -th group reaches its maximum is denoted by  $T_{mi}$ , and is a unique function of  $E_{ai}$  and  $A_i$  and the rate of heating,  $\alpha$ :

$$\frac{RT_{mi}^2}{\alpha E_{ai}} = \frac{A_i}{E_{ai}} e^{-\frac{E_{ai}}{RT_{mi}}} \quad (14)$$

Equation (14) means that if the sample is heated at the constant rate  $\alpha$ , the apex of the  $H_2S$  peak from the  $i$ -th group, which is reduced with activation energy  $E_{ai}$  and frequency factor  $A_i$ , will be different from that of the  $j$  group which is reduced with different parameters,  $E_{aj}$  and  $A_j$ .

When a mixture which contains several functional groups is reduced, the behavior of each sulfur group is similar, except that each peak will appear at a different  $T_m$ . Figure 2 shows the graph for a mixture of several groups.

The reduction curve, or the "kinetogram" can be used to derive the following data:

1. The location of  $T_{mi}$  is characteristic of the  $i$ -th functional group.
2. The integral of the peak of each group is the exact stoichiometric equivalent of the sulfur group that has been reduced. The activation energy and the frequency factor of the reaction can be determined by curve pitting of the data to equation 12.
3. Slightly different variations of this method were used by Juntgen and co-workers to study the rates of coal pyrolysis and gasification (13)(14)(15),

by Campbell and Stephen (16) to study the rates of coal pyrolysis, and by Yerger et al. (17) and Bauman et al. (18) to study the rate of evolution of  $H_2S$  during coal hydrogenation. In the latter studies, not all the sulfur was removed from the coal, therefore, quantitation of the sulfur groups cannot be done from the data. A more detailed discussion of the quantitation is presented below.

## 5.2 QUANTITATION OF THE DATA

The most important problems that should be solved so that the analysis of the sulfur groups in coal will be quantitative are:

1. COMPLETE reduction of each sulfur group.
2. COMPLETE recovery of all the  $H_2S$  from each sulfur group.

The major difficulty on the road to obtain complete reduction of the sulfur groups are mass transfer limitations. The diffusion of the reducing agent into the coal particle is slow and so is the diffusion of the  $H_2S$  out of the coal particles. These processes result in incomplete reduction of the sulfur and in the spreading of the peak from one group over a large interval of temperature. To reduce the effect of mass transfer, we used finely divided coal particles and conducted the reduction in a solvent which partially liquefies the coal. In addition, we added Co-Mo catalyst to the cell to enhance the rate of reduction of sulfur groups.

Complete recovery of all the  $H_2S$  was impossible when lignite with a large content of calcium carbonate was examined. Apparently, some of the  $H_2S$  reacted with the carbonate according to:



Most of the basic carbonates in coal, e.g., calcite, dolomite, and sidrite can, however, be easily dissolved in dilute hydrochloric acid and removed from the sample.

The application of the special solvent permitted us to reduce most of the organic sulfur below 370°C and 100 psi.

## 4. EXPERIMENTAL SYSTEM

The experimental system consists of five parts: 1) reduction cell, 2) hydrogen sulfide detectors, 3) gas flow systems, 4) heater and temperature programmer, and 5) recording and signed processing device.

Figure 3 shows the functional relation among the units. All the components except for the reduction cell are standard. Several prototypes of cells were built and tested in our laboratory. The first prototype is described in Figure 4.

One commercial detector and two modified detectors were tested: 1) the lead-acetate detector\*, 2) the flame photometric detector, and 3) electrolytic detector. The first two are differential detectors, while the third is an integral detector. The data that are reported in this manuscript were derived using the lead acetate detector.

## 5. RESULTS AND DISCUSSION

Two questions are addressed: 1. the identification peaks which belong to a specific functional group. 2. the variation in the distribution of sulfur groups in different coals.

### 5.1 IDENTIFICATION OF PEAKS

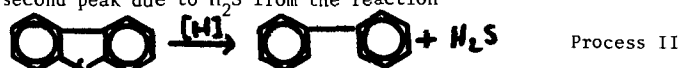
The philosophy of the identification technique is that when solids are reduced peaks that belong to a specific sulfur group will appear at the same temperature,  $T_{mi}$ , provided that the same rate of heating is used, and that the mass

\* The courtesy of Mr. C. Kimbell, President of Houston Atlas, who loaned us the equipment and helped us in its modification is greatly appreciated.

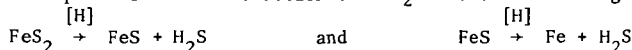
transfer does not limit the rate of reduction. Therefore, solid polymers that contain only one sulfur group, will produce one peak of sulfur only, the peak that corresponds to the sulfur group which they have. Thus, polythiophenes produce a peak which corresponds to the group  $\text{--S--}$ . Rubber produces a peak which corresponds to R-S-R and R-S-S-R, etc. Figure 5 shows the kinetogram of rubber. Figure 6 shows the kinetogram of thianthrenes. Note that two different peaks appear. The authors believe that the first peak is due to  $\text{H}_2\text{S}$  from the reaction



and the second peak due to  $\text{H}_2\text{S}$  from the reaction



The reduction of the first sulfur appear to be kinetically equivalent to the reduction of aromatic sulfides. However, the reduction of dibenzothiophene occurs at a higher temperature. The reduction of  $\text{FeS}_2$  occurs in two stages as expected:

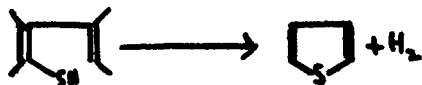


However, the "sharpness" of the peak depends on the particle size of the  $\text{FeS}_2$ . Small  $\text{FeS}_2$  produce very sharp peaks and larger  $\text{FeS}_2$  particles produce a "sluggish" peak. The FeS and Fe produce resistance to mass transfer.

## 6.2 TESTS OF COAL AND LIGNITE SAMPLES

Table 2 gives the distribution of sulfur in Illinois No. 6 coal, and in Texas lignite. Figure 7 shows the kinetogram of the Illinois No. 6 coal. A tentative assignment of functional groups to the peaks is given on the chart. Extraction of the coal with nitric acid removes the pyritic sulfur altogether, and slightly affects the organic sulfur as well. The latter is expected because nitric acid oxidizes organic sulfur to the corresponding sulfoxides (19). Figure 8 shows the kinetogram of  $\text{HNO}_3$  extracted Illinois No. 6 coal. Table 2 shows a quantitative estimate of the distribution of sulfur groups in Illinois No. 6 and in Texas lignite.

Texas lignite (Milam Co.) is more porous than bituminous coal, and therefore its resistance to mass transport is smaller than that of bituminous coal. Most of the sulfur in the samples that were tested was organic. The kinetogram in Figure 9 shows that the organic sulfur in the lignite was essentially in the form of isolated single thiophenic rings, and not in the form of dibenzothiophenes or aliphatic sulfides. This indicates that the thiophenic structures are formed in coals in early stages of the geological coalification of wood. This thiophenic structure condenses latter to dibenzothiophenic structures etc. The latter observation was unexpected, and we searched for reaction mechanisms which may lead to the same experimental observation. One such mechanism involves the reaction:



This reaction shows that isolated thiophenic structures can be produced from unstable sulfur-containing groups due to thermal decomposition. Thermally unstable sulfur groups are reduced to  $\text{H}_2\text{S}$  at much lower temperatures than stable groups, (see discussion in Ref. 6). However, if not all the unstable sulfur was reduced while the temperatures were still low, part of it may be converted into a more stable form during the analysis. Thus, if mass transfer limits the rate of reduction, the result of the analysis of coal samples will be biased, and will show a larger fraction of single-thiophenic rings.

Another observation which seems interesting is that the fraction of sulfidic sulfur is about the same in the lignite and in the bituminous coal. This observation can be accidental, however, similar results were noted by others (20).

#### 6. CONCLUSION

A method has been developed which permits to conduct detailed quantitative analysis of the distribution of sulfur groups in coal. The method permits to determine qualitatively and quantitatively the distribution of organic sulfur groups in coal samples. Illinois No. 6 bituminous coal and Texas lignite were tested, and the results are consistent with accepted theories on the sulfur in coal.

#### ACKNOWLEDGEMENT

The authors wish to thank the Office of Research and the Energy Institute of the University of Houston for their support of this program.



#### REFERENCES

1. ASTM, part 26D2492, (1974), 507.
2. British Standards Institution, BS 1016, part II (1975).
3. International Organization for Standardization, R157 (1960).
4. Attar, A., "The Fundamental Reactions of Sulfur in Coal During Pyrolysis--Review" (presented in the AIChE Meeting, Houston, March, 1977).
5. Attar, A., "The Fundamental Reaction of Sulfur and Modeling the Distribution of Sulfur in Coal Pyrolysis and Hydrogenation", Review in print in a Chemical Engineering Progress, Technical Manual.
6. Attar, A., "The Chemistry, the Thermodynamics and the Kinetics of the Reactions of the Sulfur in Coal with Gases", Accepted for publication, Fuel.
7. Attar, A. and Corcoran, W. H., "Sulfur Functional Groups in Coal", Ind. Eng. Chem., Prod. Res. Dev., 16, 168 (1977).
8. Brook, J. D., J. Inst. Fuel, 29, 82 (1956).
9. Jones, J. R., "Some Aspects of the Chemistry of Sulfur in Relation to Its Presence in Coal", Ph.D. Thesis, The Pennsylvania State University, Dept. of Fuel Technology, Sept. (1976).
10. Wandless, A. M., J. Inst. Fuel, 32, 258 (1959).
11. Horton, L. and Randall, R. B., Fuel, 26, 127 (1947).
12. Given, P. H. and Wyss, W. F., BCURA Mont. Bull., XXV(5), 165 (1961).
13. Juntgen, H., Erdol and Kohle, 17, 180 (1964).
14. Juntgen, H. and Van Heek, K. H., Fuel, 47, 103 (1968).
15. Feistel, P. P., Van Heek, K. H., and Juntgen, H., Prep. Div. Fuel Chem., 22 (1), 53 (1977).
16. Campbell, J. H. and Stephens, D. R., IBID, 21 (7) 94 (1976).
17. Yergey, A. L., Lampe, F. W., Vestal, M. L., Day, A. G., Fergusson, G. J., Johnson, W. H., Snyderman, J. S., Essenhigh, R. H., and Hudson, J. E., Ind. Eng. Chem., Proc. Res. Dev., 13 (3), 233 (1974).
18. Bauman, H., Klein, J., and Juntgen, H., Erdol and Kohle, 30 (4), 159 (1977).
19. Suter, C. M., "The Organic Chemistry of Sulfur", Wiley, N.Y. (1944).
20. Bogdanova, V. A. and Boranski, A. O., C.A. 63, 17741 (1965) and Pretezhacva, E. N. et al., C.A. 60, 6215 (1964).

Table 1: Sulfur Classes in Illinois #6 and in Texas Lignite

	Illinois #6	Texas Lignite
Total Sulfur	4.05	1.03
FeS <sub>2</sub> wt%	1.56	0.19
SO <sub>4</sub> wt%	0.38	0.07
Organic wt%	2.09	0.77

Table 2: Wt% of the Organic Sulfur in Different Functional Groups  
Tentative assignment. ±15% error is possible.

Structure	Illinois No. 6 (Bituminous)	Texas Lignite
-SH	present in small amounts	
aliphatic or alicyclic 	27.4	26.6
-S- or 		
Dibenzothiophenic	41.8	16.3
Single thiophenic or other very stable group.	30.8	57.1

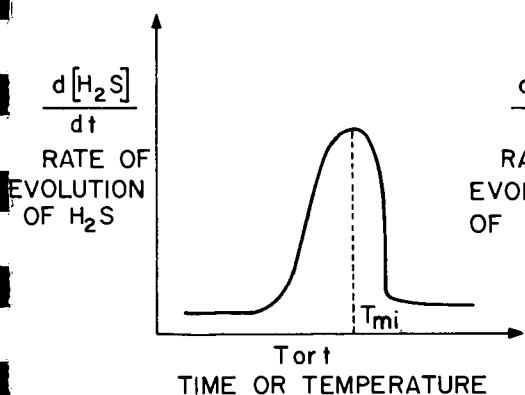


FIGURE 1: ANALYSIS OF MATERIAL WITH A SINGLE FUNCTIONAL GROUP

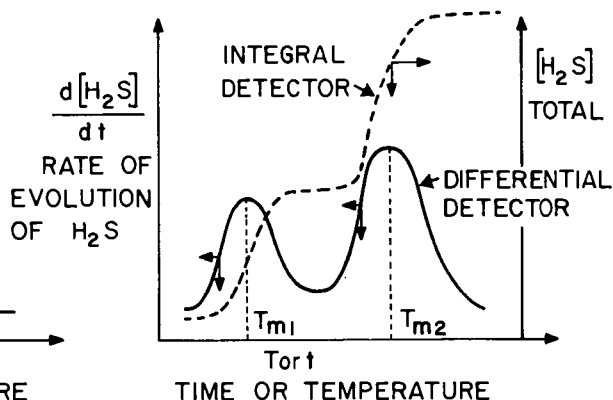


FIGURE 2: ANALYSIS OF A MIXTURE CONTAINING TWO GROUPS USING A DIFFERENTIAL AND AN INTEGRAL DETECTORS.

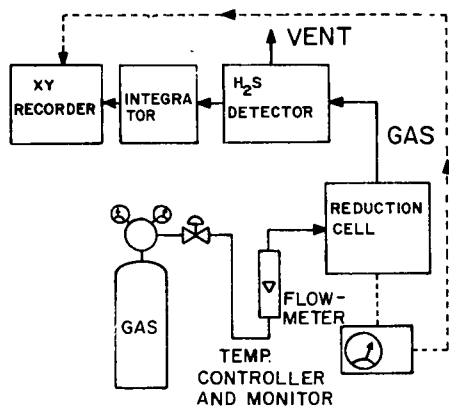


FIGURE 3: SCHEMATIC DIAGRAM OF EXPERIMENTAL SYSTEM.

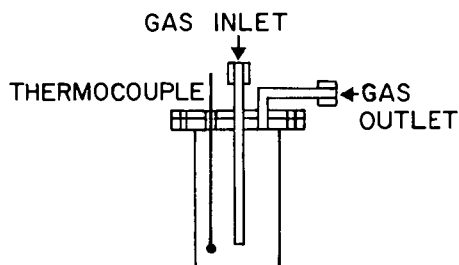


FIGURE 4: PROTOTYPE OF REDUCTION CELL.

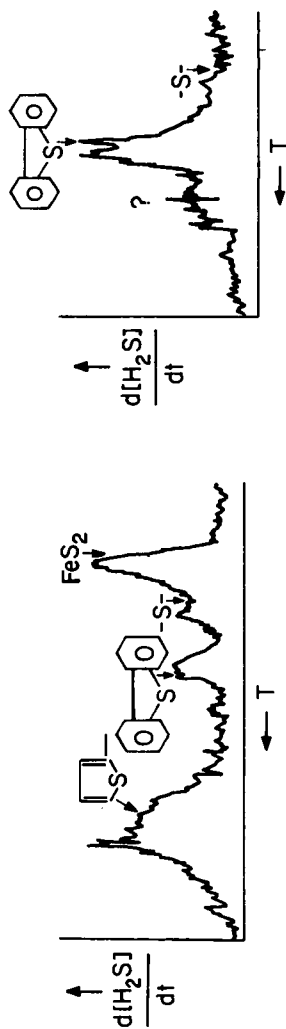


FIGURE 7: KINETOGRAM OF 32.6 mg ILLINOIS No. 6 BITUMINOUS COAL. THE GROUP ASSIGNMENT IS TENTATIVE.

FIGURE 8: KINETOGRAM OF ILLINOIS No. 6 - EXTRACTED WITH  $HNO_3$ .

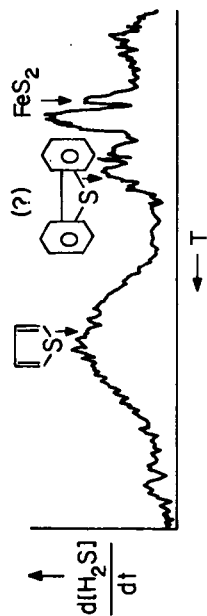


FIGURE 9: KINETOGRAM OF TEXAS LIGNITE. THE GROUP ASSIGNMENT IS TENTATIVE.



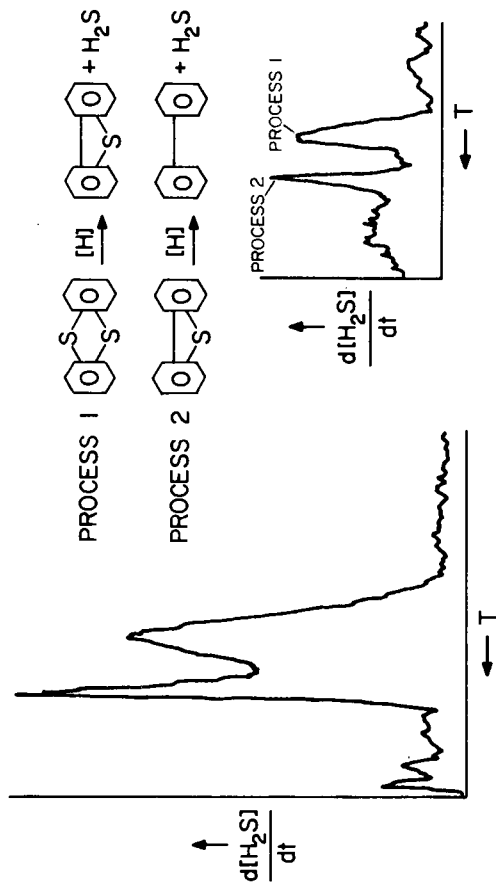


FIGURE 5: KINETOGRAM OF RUBBER.

FIGURE 6: KINETOGRAM OF THIANTHRENE.

## The Aliphatic Structures in Coal

N. C. Deno, Barbara A. Greigger, and Stephen G. Stroud

Department of Chemistry, The Pennsylvania State University  
University Park, Pennsylvania 16802

Coals are varying and complex in their chemical structures. This type of situation is classically studied by degradative procedures which reduce the complexity to simpler component parts. This has been done with coal and four degradative methods have emerged to which we owe much of our concepts of coal structure. These are (a) destructive distillation of coal to benzene and pyridine derivatives, (b) alkyl transfer to phenol and determination of the alkylphenols, (c) liquifaction or solvent refining which reduces MW from the 5000 to 600 range, and (d) oxidation with the usual oxidizing agents ( $\text{HNO}_3$ ,  $\text{O}_2$ , Mn VII, Cr VI) to produce benzene carboxylic acids.

We now introduce a 5th degradation procedure. This is oxidation with  $\text{H}_2\text{O}_2$  in TFA (trifluoroacetic acid) with or without addition of  $\text{H}_2\text{SO}_4$ . This system has the capability of completely dissolving coal to form colorless or pale brown solutions in which all aromatic structures have been destroyed and most of the aliphatic structures preserved (1,2). The nature of its action is illustrated by three examples. Treatment of propylbenzene, isopropylbenzene, and 1,2-diphenylethane by the usual oxidizing agents ( $\text{HNO}_3$ ,  $\text{O}_2$ , Mn VII, Cr VI) leads to attack at the benzylic positions, oxidative cleavage, and formation of benzoic acid. In contrast, the  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  oxidations attack the aromatic rings leaving the benzylic positions virtually untouched even when tertiary as in isopropyl and cyclohexyl benzenes. The products from the three examples are respectively butyric acid, isobutyric acid, and succinic acid (2). It is immediately evident that this new degradation procedure is particularly suited to cataloging and categorizing the aliphatic structures in coals.

The products from the  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  oxidations have been examined in two ways. The nmr (nuclear magnetic resonance) spectra of the reaction mixture provides an inventory of the hydrogen present in the products. Acetic acid, succinic acid, and methanol (as the trifluoroacetate) can be easily recognized because they generate sharp singlets and because they are dominant products. The absolute yields were determined using malonic acid as an internal standard. The non-volatile products can be isolated by evaporation in vacuo, conversion to methyl esters, and examination by nmr and gc (gas chromatography).

It must be emphasized that there has not been sufficient time or funding to optimize and standardize procedures. However, it has been found that acetic acid is produced from a wider variety of models in  $\text{H}_2\text{O}_2$ -TFA oxidations than in  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  oxidations. In the latter, acetic acid formation is mainly limited to arylmethyl groups. The current procedure is to add 0.8 g of <20 mesh coal to a mixture of 12 ml of TFA, 15 ml of 96%  $\text{H}_2\text{SO}_4$ , and 15 ml of 30% aq.  $\text{H}_2\text{O}_2$ . Addition is exothermic, but not enough to require any precautions with the above amounts. The mixture is heated for five hours at 60°. After cooling, it is important to destroy excess peroxide with 10% Pt on asbestos until  $\text{O}_2$  evolution ceases and a KI test for peroxide is negative.

Table I summarizes data on products from oxidations of coal. Table II summarizes data on model compounds. The data has been submitted for publication in greater detail (2).

Despite the preliminary nature of the data, several conclusions are possible. No propionic acid, butyric acid, or isobutyric acid were observed in the products from any of the coals. This eliminates structures involving ethyl, propyl, and

Table I. NMR Spectra of Solutions of Coals in H<sub>2</sub>O<sub>2</sub>-TFA-H<sub>2</sub>SO<sub>4</sub>

Coal	H Obsvd. x 100/Total H in Coal			
	Acetic acid (2.18 $\delta$ )	Succinic acid (2.78 $\delta$ )	alkyl other than $\alpha$ or $\beta$ (0-2.0 $\delta$ )	Other bands
Pittsburgh Seam	1.0	3.3	0	3.5
79.5% H 5.2% H				
Illinois #6	5.7	8.9	0.5	2.6
70.5% C 5.1% H				
Illinois #6 Monterey	2.8	8.9	2.2	4.1
69.7% C 4.98% H				
Illinois #6 Monterey solvent refined	4.4	2.4	1.0	2.8
Wyodak solvent refined	2.3	1.0	8.1	5.9
87.0% C 6.6% H				
Lignite North Dakota	0	10.6	50.6	20.4 <sup>a</sup>
65.3% C 4.4% H				

<sup>a</sup> This was entirely methanol as its trifluoroacetate.

Table II. H<sub>2</sub>O<sub>2</sub>-TFA-H<sub>2</sub>SO<sub>4</sub> Oxidations of Model Compounds

Compound	Predominant Product(s)	% Yield <sup>a</sup>
1,2-diphenylethane	succinic acid	73
9,10-dihydrophenanthrene	succinic acid	71
acenaphthene	succinic acid	64
indan	succinic acid	27
5-hydroxyindan	succinic acid	38
4,7-dimethylindan	succinic acid <sup>b</sup>	
	acetic acid <sup>b</sup>	
toluene	acetic acid	68
1,4-dimethylbenzene	acetic acid	66
1,3-dimethylbenzene	acetic acid	66
1,2-dimethylbenzene	acetic acid	46
ethylbenzene	propionic acid	71
propylbenzene	butyric acid	73
isopropylbenzene	isobutyric acid	32
t-butylbenzene	(CH <sub>3</sub> ) <sub>3</sub> CCOOH	
cyclohexylbenzene	c-C <sub>6</sub> H <sub>11</sub> COOH	
methoxybenzene	methanol	79
3-phenyl-1-propanol	butyrolactone	75
tetralin and 6-hydroxytetralin	cyclohexene-1,2-(COOH) <sub>2</sub>	69
1,3-diphenylpropane	glutaric acid	

<sup>a</sup> Computed on the basis of one mol of substrate yields one mol of product except for the three dimethylbenzenes where the basis was 2 mols of acetic acid from one mol of substrate.

<sup>b</sup> Acetic acid : succinic acid = 1.1.

isopropyl attached to an aryl ring. These structures have been reported previously (3,4). While our results will be more reliable if confirmed by gc studies, they seem reasonably firm now. Furthermore, the past reports are in some doubt because they depended on Friedel-Crafts type of degradations (3) or tenuous analysis of broad absorption bands in nmr spectra of coal extracts (4).

None of the bituminous coals contained arylmethoxy as shown by the complete absence of methanol in the oxidation products. This agrees with results of Zeisel determinations which also showed no methoxyl (5). This is particularly interesting because lignite and lignin are well-known to contain arylmethoxy groups. In fact an  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  oxidation of lignin at  $25^\circ$  showed 14.0% by weight arylmethoxy which is typical for lignins (6-8). A sample of North Dakota lignite showed 9.6% arylmethoxy. Both yields were computed on the basis that each arylmethoxy went quantitatively to methanol. Neither lignin nor lignite produced acetic acid confirming the well-established absence of aryl methyl groups (6-8). Both produced succinic acid indicating unsubstituted  $\text{ArCH}_2\text{CH}_2\text{-C}$  components in the structure.

All coals produced acetic acid, but in widely varying amounts. The model studies indicate that this acetic acid comes from arylmethyl groups and the amount of arylmethyl can be estimated from the data in Table I. In making this estimate, it should probably be assumed that the yield of acetic acid from each arylmethyl is ~70% based on the models in Table II.

The succinic acid originates from diarylethane or indan structures. Since any indan components in coal would likely have alkyl, alkoxy, or hydroxy groups on the aryl ring, it was of particular concern to us to show that such substituents did not significantly alter the production of succinic acid. For this purpose both 4,7-dimethylindan and 5-hydroxyindan were studied and both gave succinic acid as the dominant product the same as indan itself.

The question remains as to whether the succinic acid arises from indan or diarylethane structures or from some other type of structure which has not been studied. One bit of evidence is suggestive that indans are predominantly responsible for succinic acid formation. Oxidation of indan with  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  gave no acetic acid whereas the amounts of acetic and succinic acids were comparable when  $\text{H}_2\text{O}_2$ -TFA was the oxidizing agent. Pittsburgh Seam and Illinois #6 coals showed similar effects. Leaving out the  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}_2$ -TFA oxidations caused the yield of acetic acid to more than double (2).

No aryl hydrogen appeared in the oxidation products despite the fact that benzoic acid is inert. This eliminates benzoate esters as components of coal structure.

The absence of cyclohexene-1,2-dicarboxylic anhydride shows that no tetralin structure can be present of the type which are unsubstituted on the aliphatic ring.

The solvent refining (liquifaction) of coal is thought to involve thermal cleavage of benzyl ethers and conversion of the benzyl radicals to arylmethyl by hydrogen abstraction (9-11). The data on Monterey Coal in Table I is in accord with this view in that the yield of acetic acid (reflecting arylmethyl) increased. The yield of succinic acid decreased presumably reflecting the aromatization or desaturation of indan, diarylethane, and partially reduced aromatic structures.

There is much to do in this field in the direction of varying the oxidation technique to make it more selective and to increase yields. Furthermore, no start has been made in identifying the other products of  $\text{H}_2\text{O}_2$ -TFA- $\text{H}_2\text{SO}_4$  oxidations although their aliphatic nature, small size, and simple nmr spectra suggests that their identification is facile.

The total  $\%H$  observed can be calculated by adding the columns in Table I. The highest was 81.9% for North Dakota Lignite and the lowest was 7.8% for Pittsburgh Seam Coal. This largely reflects the aromaticity of the coal. The aromatic hydrogens are completely lost while the aliphatic are largely preserved. However, even in model compounds loss of 30% of the aliphatic H was typical and the loss is even greater in certain aliphatic structures such as those on benzyl derivatives. Thus, while the  $\%H$  observed in a typical bituminous coal such as Illinois #6 is a respectable 17.7%, this represents no more than about half of the total aliphatic hydrogen.

We are deeply indebted to Dr. Malvina Farcasiu and Dr. Duayne Whitehurst for the last 4 substrates in Table 1, for a sample of lignin, and for stimulating discussions. They will be coauthors with us in future papers on solvent refined coal and on lignin. We are also deeply indebted to Mr. Philip Dolsen and the Coal Research Station at The Pennsylvania State University for the first two substrates in Table I. Complete analyses of these coals are available (2). We also wish to acknowledge stimulating discussions with Dr. Ron Liotta of Exxon Corp., Linden, New Jersey.

#### References

- (1) N. Deno, B. A. Greigger, L. A. Messer, M. D. Meyer, and S. G. Stroud, *Tetrahedron Lett.*, 1977, 1703.
- (2) N. Deno, B. A. Greigger, and S. G. Stroud, submitted to *Fuel*.
- (3) L. A. Heredy, A. E. Kostzo, and M. B. Neuworth, *Fuel* 1965, 44, 125.
- (4) K. D. Bartle, T. G. Martin, and D. F. Williams, *Fuel* 1975, 54, 226.
- (5) D. W. van Krevelen, "Coal," Elsevier Publishing Co., Amsterdam, 1961.
- (6) "Lignin Structure and Reactions," *Advances in Chemistry Series No. 59*, Am. Chem. Soc., Washington, D. C., 1966.
- (7) W. J. Schubert, "Lignin Biochemistry," Academic Press, N. Y., 1965.
- (8) F. E. Brauns and D. A. Brauns, "The Chemistry of Lignin," Academic Press, N. Y., supplemental vol. 1960.
- (9) R. G. Roberts, D. C. Cronauer, D. M. Jewell, and K. S. Seshadri, *Fuel* 1977, 56, 17.
- (10) B. S. Ignasiak and M. Gawlak, *Fuel* 1977, 56, 216.
- (11) D. D. Whitehurst, M. Farcasiu, T. O. Mitchell, and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," Mobil Research and Development Corp., Princeton, N.J., July 1977, report submitted to Electric Power Research Institute.

# CHROMATOGRAPHIC SEPARATION OF COAL LIQUIDS

By

T. E. Cogswell and D. R. Latham

Laramie Energy Research Center  
P. O. Box 3395  
Laramie, Wyo. 82071

## INTRODUCTION

Coal liquefaction is a major attempt to meet certain energy requirements and at the same time protect the environment. If coal liquefaction is to be successful, a technology must be developed that provides analytical data on both feed coals and liquid products. Refining procedures could then be altered to accommodate syncrudes of different composition. Thus, efficient processing and utilization require a knowledge of the chemical composition of coal liquids.

Interest in the chemical structure of coal and coal conversion products has increased greatly in recent years. This interest has produced two general approaches to the study of coal liquids. One is the detailed characterization of a particular coal liquid by extensive separation followed by elaborate spectroscopic characterization of the various compound types (1). The other approach emphasizes a rapid and simple method of separation in which fewer fractions are generated (2). The latter is more amenable to on-stream control, where fast procedures are required.

Our approach to the analysis of coal liquids incorporates the most attractive features of the two approaches. Five chemically meaningful fractions are generated from a total coal liquid. These fractions are separated on a chemical functionality basis and are suitable for detailed characterization. Asphaltene and pre-asphaltene fractions are purposefully avoided because of their lack of chemical definition.

This paper describes the separation of a coal liquid into five fractions by liquid chromatography. The fractions are generated by ion exchange, coordination complex, and adsorption chromatography. The nonhydrocarbon fractions account for most of the coal liquid and were emphasized in the characterization work that is reported here.

## EXPERIMENTAL

### Coal Liquid Sample

The coal liquid used in this investigation was obtained from the Pittsburgh Energy Research Center's Synthoil process (3). The feed was a high-sulfur West Virginia coal slurried in 65 percent product recycle oil. The process used a 14-ft catalytic reactor operated at 450°C and 4000 psig of hydrogen. The liquid product was centrifuged to reduce water and solids.

### Apparatus

Infrared spectra were recorded using a Perkin-Elmer 621\* infrared spectrophotometer; low-resolution mass spectra were recorded on a Varian CH-5 single-focusing mass spectrometer. The columns used for chromatographic separations were similar to those used by Jewell et al. (4). They were gravity flow columns, 1.4-cm i.d. by 119-cm, with a recycling arrangement that permits the continuous elution of the sample without the need for large quantities of solvent.

## Reagents

All solvents were flash distilled. The ion-exchange resins and other chromatographic materials were prepared according to previously reported methods (5).

## Routine Methods of Nitrogen, Sulfur, and Oxygen Analyses

Elemental analyses were performed at a commercial laboratory; nitrogen was determined by the micro-Dumas method; sulfur, by combustion followed by titration of oxidation product with barium perchlorate to a colorimetric endpoint; and oxygen, by a modified Unterzaucher method.

## Quantitative Infrared Analyses

Quantitative infrared measurements and calculations were performed in a manner similar to that used by McKay et al. (6).

## Separation Procedure

The coal liquid (0.5 g) was dissolved in methylene chloride (20.0 ml) and passed through a 10- to 15-micron filter to remove inorganic solids and any undissolved organics. The material retained on the glass filter amounted to less than 2 percent of the total coal liquid. The separation was performed by sequentially passing the coal liquid through four chromatographic columns to obtain five fractions: acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons as shown in Figure 1.

Separation of Acids--Anion Exchange Chromatography. - The sample of filtered coal liquid was chromatographed on anion resin (100 g) that had been wet packed in the column with methylene chloride. Unreactive material was washed from the resin with methylene chloride (700 ml) for 3 hours or until the eluant was clear. After the unreactive materials were removed, the reactive compounds (acids) were recovered in two steps. The column was first eluted with 60% benzene-40% methanol (350 ml); the resin was then removed from the column and placed in an extractor; the remaining acid was removed by elution with 60% benzene-40% methanol (350 ml) saturated with carbon dioxide.

Separation of Bases--Cation Exchange Chromatography. - The sample of acid-free coal liquid (about 350 mg) was taken to dryness by evaporation under a nitrogen atmosphere and redissolved in benzene (25 ml). The benzene solution was chromatographed on cation resin (50 g) that had been wet packed in the column with benzene. Unreactive material was eluted from the resin with benzene (500 ml) for 1 hour or until the eluant was clear. The reactive material (bases) was removed from the resin in two steps. The column was first eluted with 60% benzene-40% methanol (350 ml); the resin was then removed from the column and placed in an extractor; the remaining bases were removed from the resin with 54% benzene-38% methanol-8% isopropylamine (200 ml).

Separation of Neutral Nitrogen Compounds--Ferric Chloride Coordination Chromatography. - Ferric chloride-Attapulugus clay (80 g) was placed above anion resin (120 g) in a single column. After the column was washed with cyclohexane (100 ml), the acid- and base-free material, freed of benzene and redissolved in cyclohexane (50 ml), was passed through the column. The column was eluted with cyclohexane (300 ml) to remove hydrocarbons. The nitrogen compound-ferric chloride complexes were removed from the clay with 1,2-dichloroethane (200 ml). These complexes were subsequently broken by passing the solution over the anion resin; the ferric chloride salt was retained on the resin, and the neutral nitrogen compounds were recovered in the eluate.

Separation of Hydrocarbons--Silica Gel Chromatography. - The acid-, base-, and neutral-nitrogen-free coal liquid, freed of cyclohexane and redissolved in n-pentane (50 ml), was placed on a silica gel column (150 g). The column was eluted with n-pentane (approximately 500 ml or until UV monitor showed absorbance greater than 10 percent of full scale at 254 nm) to remove the saturate hydrocarbons. The aromatic hydrocarbons were then recovered by elution with benzene (approximately 300 ml).

## RESULTS AND DISCUSSION

Recovery and precision data for three different runs are presented in Table 1. Recoveries from 96 to 98 percent may be expected from the separation scheme. The precision data in the last column of Table 1 show a reproducibility of  $\pm 3$  wt. percent for each of the five fractions.

TABLE 1. - Three separations showing weight percent and precision for each fraction

Fraction	Weight percent			Precision
	Run 1	Run 2	Run 3	
Acid	27	33	31	30 $\pm$ 3
Base	20	18	22	20 $\pm$ 2
Neutral nitrogen	12	10	11	11 $\pm$ 1
Saturate	10	13	11	11 $\pm$ 2
Aromatics	27	22	23	24 $\pm$ 3
Recovery	96	96	98	97 $\pm$ 1

The data in Table 1 show that for each separation run the acids, bases, and neutral nitrogen compounds represent about 60 percent of the total coal liquid. Acids and bases alone amount to about 50 percent of the total liquid showing the highly polar nature of the coal liquid. This relatively high amount of polar material compared with amounts found in petroleum poses problems in developing separation methods and in processing these liquids into useful fuels.

The saturate and aromatic hydrocarbon fractions represent about 35 percent of the total liquid. The content of aromatic hydrocarbons is about twice that of saturate hydrocarbons, reflecting the aromatic character of the coal feedstock.

Elemental analyses in Table 2 show that oxygen and nitrogen are the primary heteroatoms present in the polar fractions. The acid fraction contains about 5 percent oxygen, primarily due to large amounts of phenolic compounds as discussed later. The bases are high in nitrogen, having about 4 percent nitrogen. Reproducible data for the neutral nitrogen fraction were not obtained so they are not included in Table 2. The saturate hydrocarbons contain only small amounts of heterocompounds, but the aromatic hydrocarbons contain large amounts of oxygen heterocompounds. The aromatic fraction shows 3.4 percent oxygen, which is high for a hydrocarbon fraction. This might be explained by the presence of furan or dibenzofuran-type oxygen compounds that are not removed by the resins or the ferric chloride. Data on sulfur are too limited to determine whether sulfur is evenly distributed among the fractions or whether sulfur compounds are concentrated in any one fraction(s). Molecular-weight data on the total coal liquid and on selected fractions from the separation show average molecular weights ranging from 210 to 250.



TABLE 2. - Elemental analyses and molecular weights of Synthoil and fractions

Sample	Weight percent					Molecular wt.
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	LRMS*
Total Synthoil	86.09	7.4	1.6	3.9	0.7	225
Acid	79.4	6.7	1.0	5.5	0.8	250
Base	81.5	7.4	3.9	1.9	-	225
Saturates	88.1	11.6	0.3	-	-	230
Aromatic	87.6	7.6	0.1	3.4	0.6	210

\*Low-resolution mass spectrometry.

#### Characterization of Acid Fraction

The acid fraction represents about 30 percent of the total coal liquid. This fraction has 5.5 percent oxygen (Table 2) and an average molecular weight of 250. Calculations from these data, assuming one oxygen atom per molecule, show that 86 percent of the molecules contain one oxygen atom. Similarly, one percent nitrogen and a molecular weight of 250 calculates to 15 percent of the molecules containing one nitrogen atom.

The infrared spectrum of the acid fraction, Figure 2, shows a strong band of free phenolic O-H stretching vibration at  $3590\text{ cm}^{-1}$ . The lack of significant absorption in the carbonyl region ( $1650\text{--}1750\text{ cm}^{-1}$ ) indicates the absence of carboxylic acids. Quantitative infrared analysis shows that approximately 85 percent of the fraction is represented by the phenolic O-H stretching band. The remaining material can be accounted for by quantitative analysis of the N-H absorption at  $3460\text{ cm}^{-1}$ , showing the presence of pyrrolic nitrogen compounds.

Two different methods give the same values for oxygen compounds (phenols) and for nitrogen compounds (pyrroles). Thus, the elemental analysis suggests 86 percent oxygen compounds, and infrared shows that these compounds, 85 percent of the fraction, are phenols. Similarly, elemental analysis shows 15 percent nitrogen compounds and infrared shows about the same amount of pyrrolic nitrogen compounds.

#### Characterization of Base Fraction

The base fraction represents about 20 percent of the coal liquid. A nitrogen content of almost 4 percent reflects a successful attempt to concentrate nitrogen compounds. From the average molecular weight and the nitrogen content it appears that about 70 percent of the molecules contain one nitrogen atom. This is not as easy to substantiate with infrared spectroscopy as it was in the acid fraction. The problem results from overlapping bands, as shown in Figure 3. Pyrrolic N-H stretching at  $3460\text{ cm}^{-1}$  overlaps with amide-type N-H stretching at  $3410\text{ cm}^{-1}$ , prohibiting quantitative determinations by infrared spectrometry. The infrared spectrum shows carbonyl absorption in the region  $1650\text{--}1700\text{ cm}^{-1}$ , which may be due to small amounts of amides. A shoulder on the low-frequency side of the  $1600\text{ cm}^{-1}$  band may indicate the presence of pyridines in this fraction.

#### Neutral Nitrogen Fraction

This fraction represents only about 10 percent of the total coal liquid. The infrared spectrum of this fraction is given in Figure 4. The spectrum shows an absorption band at  $3460\text{ cm}^{-1}$  due to pyrrolic N-H stretching vibrations and a shoulder around  $3410\text{ cm}^{-1}$  probably due to N-H stretching of amide types. Carbonyl absorption between  $1700$  and  $1750\text{ cm}^{-1}$  also suggests the presence of amides.

### Saturate Hydrocarbon Fraction

Saturated hydrocarbon compounds comprise 11 percent of the total coal liquid and less than one-third of the total hydrocarbon material. A gas chromatogram of this fraction is presented in Figure 5. The figure shows that normal paraffins, ranging in carbon number from 13 to 35, are major components of this fraction.

### Aromatic Hydrocarbon Fraction

About one-fourth of the total coal liquid is defined by the separation method as the aromatic hydrocarbon fraction. However, this fraction has been shown to have over 3 percent oxygen. The compound types containing oxygen have not been defined in this work. Calculations using 3.4 percent oxygen and an average molecular weight of 210, assuming one oxygen atom per molecule, show that about 45 percent of the molecules contain oxygen. This oxygen is probably of the furan or dibenzofuran type which is nonreactive to resins or ferric chloride. Thus, these compounds are isolated with aromatic hydrocarbons in the final separation step.

### SUMMARY

A Synthoil coal liquid that had not been solvent deasphalted was separated into fractions of acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons using ion exchange, coordination, and adsorption chromatography. The separation method is reproducible, and recovery of material was better than 95 percent. The method separates compounds according to chemical functionality and generates fractions that are suitable for detailed characterization. The Synthoil coal liquid used in this investigation contains about 30 percent acids and 20 percent bases, according to the ion exchange resin definition of acids and bases. The acids were characterized as being about 85 percent phenolic compounds and 15 percent compounds containing pyrrolic nitrogen. The bases were found to be largely pyridine and pyrrolic nitrogen compound types. The saturate hydrocarbons were 11 percent of the total coal liquid, and the aromatic hydrocarbons were about 24 percent; however, oxygen compounds, probably of the dibenzofuran type, were also found in the aromatic hydrocarbon fraction. The average molecular weight of the coal liquid sample was determined by low resolution mass spectrometry to be about 225.

### CONCLUSIONS

This separation method, a modification of a previous method, may be useful for separating other coal liquids according to chemical functionality. An important advantage of this method over other separation schemes used for coal liquids is that the total coal liquid is separated and a minimum number of fractions is generated. A practical application of the separation scheme may be found in monitoring the amounts of acids and bases produced in coal liquification processes. Such information is important because acids and bases are known to cause both chemical and physical problems in the processes.

### REFERENCES

1. T. Aczel, R. B. Williams, R. J. Pancirov, and J. H. Karchmer, "Chemical Properties of Synthoil Products and Feeds," report prepared for U.S. Energy Research and Development Administration, FE 8007, 1977.
2. J. E. Schiller and D. R. Mathiason, *Anal. Chem.* **49**, 1225 (1977).
3. S. Akhtar, N. J. Mazzocco, M. Weintraub, and P. M. Yavorsky. "Synthoil Process for Converting Coal to Nonpolluting Fuel Oil," presented at Fourth Synthetic Fuels from Coal Conference, Oklahoma State University, Stillwater, Okla. May 6-7, 1974.

4. D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, *Anal. Chem.* 44, 1391 (1972).
5. J. F. McKay, P. J. Amend, T. E. Cogswell, P. M. Harnsberger, R. B. Erickson, and D. R. Latham, *Preprints, Div. Petrol. Chem., ACS*, 22, (2), 708 (1977).
6. J. F. McKay, T. E. Cogswell, J. H. Weber, and D. R. Latham, *Fuel* 54, 50 (1975).

\*Mention of specific brand names or models of equipment is made for identification only and does not imply endorsement by the Department of Energy.

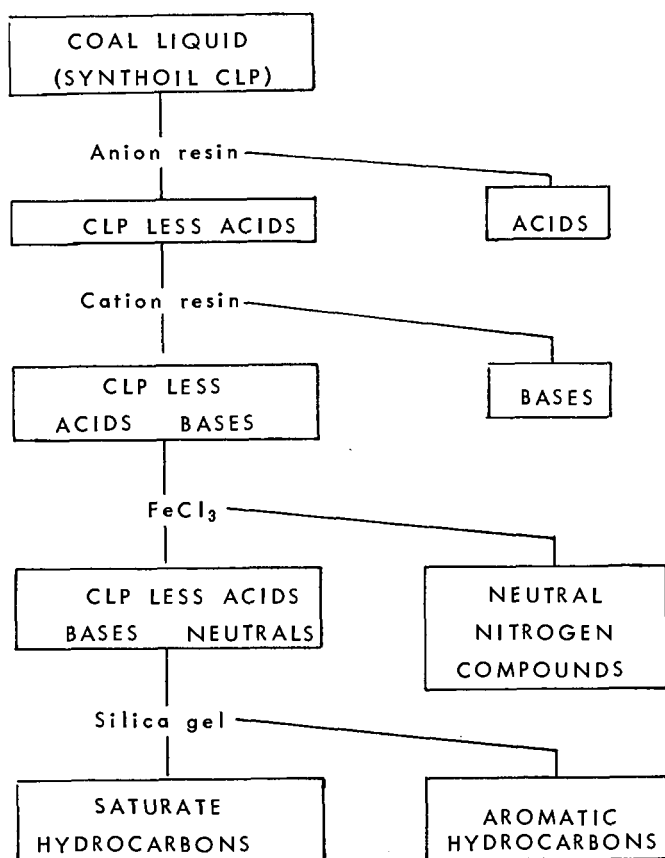


Figure 1- SEPARATION PROCEDURE

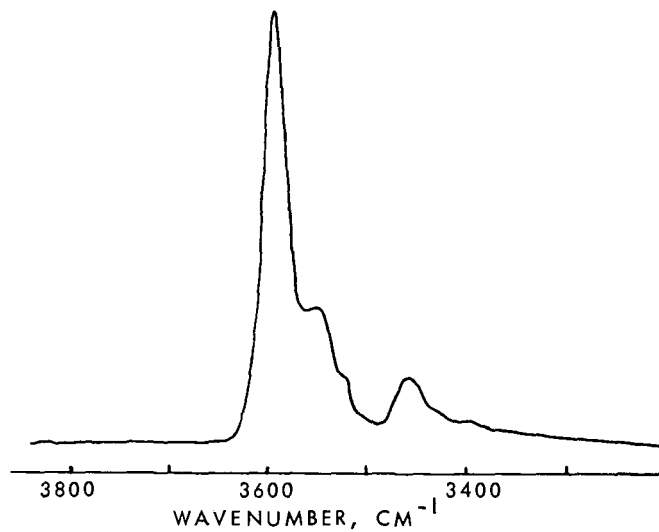


Figure 2- PARTIAL INFRARED SPECTRUM OF ACID FRACTION

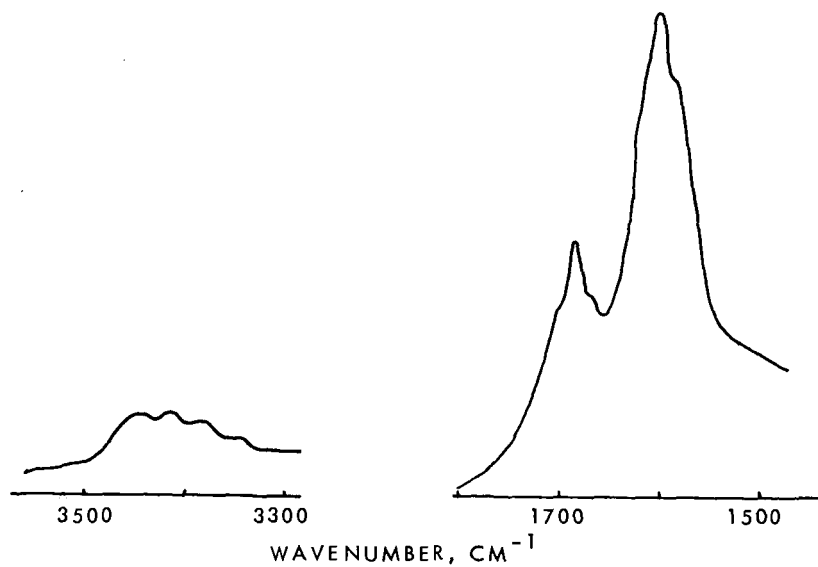


Figure 3 - PARTIAL INFRARED SPECTRUM OF BASE FRACTION

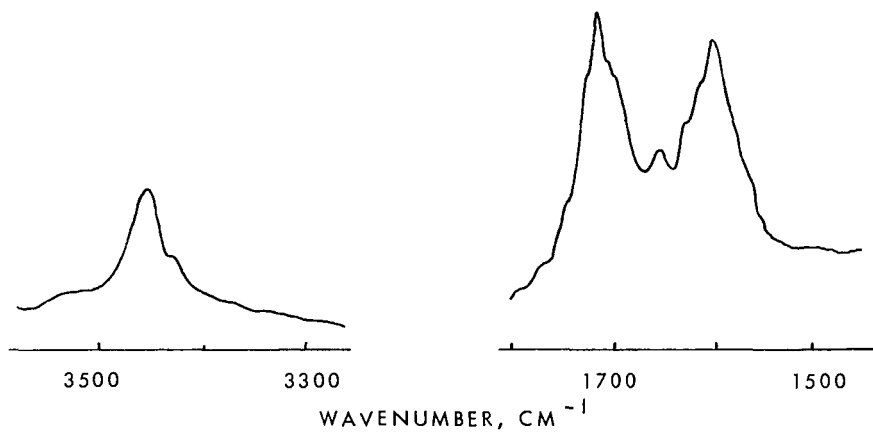


Figure 4 - PARTIAL INFRARED SPECTRUM OF NEUTRAL NITROGEN FRACTION

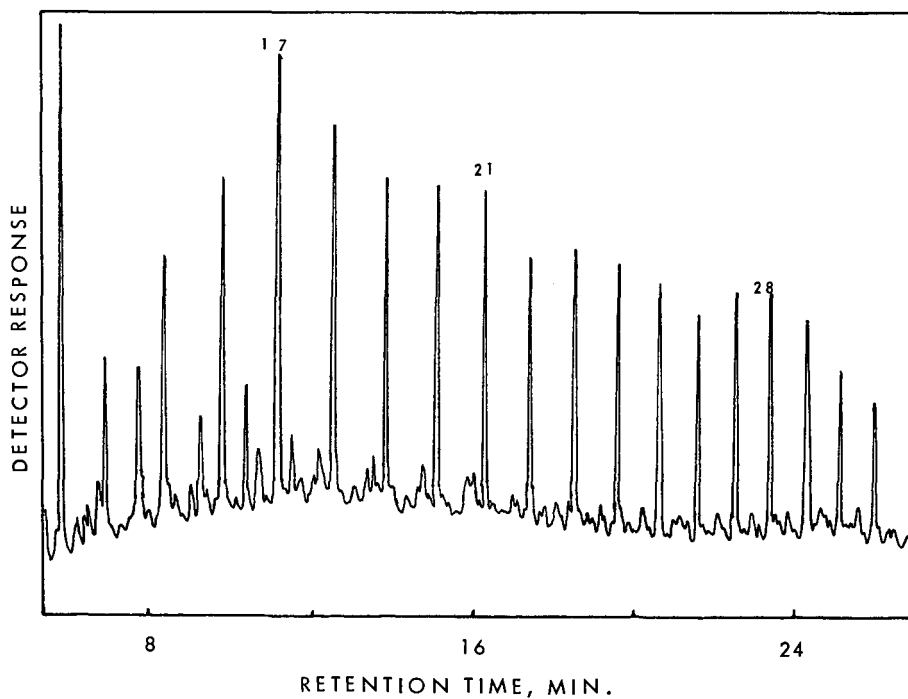


Figure 5 - GC CHROMATOGRAM OF SATURATE FRACTION

CO-Steam Process: Functional Group Analysis of  
Non-Distillables in Lignite-Derived Liquids

Bruce W. Farnum and Curtis L. Knudson

Grand Forks Energy Research Center  
Grand Forks, North Dakota 58202

The CO-Steam process for conversion of lignite to boiler fuel consists of reaction of a finely ground slurry of lignite in hydrocarbon donor solvent with carbon monoxide and hydrogen at about 450° C and pressures up to 5000 psi (1). Recent studies at the Grand Forks Energy Research Center (GFERC) have utilized a preheated batch autoclave with gas and slurry phase sampling to establish optimum reaction conditions for reduction in molecular weight of the non-distillables in CO-Steam product (2,3). A study of the effect of the nature and quantity of non-distillables on coal liquid viscosity has pointed out the importance of reducing the quantity and molecular weight of non-distillables (4). This study also pointed out a relationship between weak acid concentration and percent oxygen in non-distillables, and product quality as indicated by solution viscosity.

CO-Steam products were separated into four fractions based on solubility in hexane, toluene, and tetrahydrofuran. The acidity of each fraction was determined by non-aqueous titration with tetramethyl ammonium hydroxide. The end point obtained indicated total oxygen acids (phenols) plus nitrogen acids (carbazoles). Table 1 lists the weight percent of each solubility fraction, and their measured acidities. Close agreement was obtained between measured acidities of total products and weighted sums of the acidities of the individual fractions. CO-Steam products A and B were produced in continuous reactors at Pittsburgh Energy Research Center using recycled CO-Steam oil as the slurry vehicle, while CO-Steam C was produced in our batch autoclave using 9:1 anthracene oil - tetralin as vehicle. Higher acidity of the oil fractions of A and B can be attributed to the buildup of phenols content during recycle of the solvent. Higher acidity of the other fractions of A and B can be partially explained by their higher molecular weight resulting from lower processing temperature. Figure 1 illustrates the relative acidity of the CO-Steam fractions in Meq H<sup>+</sup> per fraction per gram of total product.

CO-Steam products were separated by column chromatography on alumina into three fractions using a simplification of the method of Schiller and Mathiason (5). Fraction 1 (eluted by toluene) consisted of hydrocarbons, fraction 2 (eluted by chloroform, 1% ethanol) consisted primarily of nitrogen compounds, and fraction 3 (eluted by 9:1 tetrahydrofuran - methanol) consisted primarily of hydroxyl compounds as confirmed by mass spectrometry of the volatile constituents. Acid and base titrations confirmed the absence of acid-base reactivity in the hydrocarbon fractions. The nitrogen compound fractions were more acidic and more basic than the hydroxyl fractions, indicating the concentration of nitrogen acids and bases in fraction 2.

A matrix of parameters was developed to provide separate estimates of oxygen acids and nitrogen acids content from non-aqueous titration and elemental analysis data, regardless of mineral content of the sample. When applied to a set of SRCs and CO-Steam distillation residues, it was found that oxygen acids decreased linearly with molecular weight by gel permeation high pressure liquid chromatography, while nitrogen acids remained at a constant concentration (Figure 2). When model solutions were prepared from the SRCs and CO-Steam distillation residues with anthracene oil, it was found that log viscosity of 25 percent solutions decreased linearly with acidity due to oxygen acids, as well as total acidity in a parallel fashion. The constant difference in curves represents the unchanging concentration of nitrogen acids, despite the varying degree of depolymerization represented in the range of samples. These results imply that during coal

depolymerization: (1) the stable core of a preasphaltene or asphaltene molecule includes a carbazole, benzocarbazole, dibenzocarbazole or related nitrogen acid, and (2) extended processing to lower molecular weight (and thus lower viscosity) involves scission of bonds linking a phenolic oxygen acid to the stable core of the molecule. The calculation method is summarized as follows:

% Basic N = 1.4 B  
 % Acidic N = 100 N - 1.4 B  
 % Acidic O = 1.6 A - 16/14 (100 N - 1.4 B)  
 % Neutral O = 100 X - (1.6 A - 16/14 (100 N - 1.4 B))

where:

A = (meq acid/g sample) -- by non-aqueous titration.  
 B = (meq base/g sample) -- by non-aqueous titration.  
 N = (g nitrogen/g sample) -- by Kjeldahl method.  
 X = (g oxygen/g sample) -- by Neutron Activation Analysis.

Assumptions:

Neutral N = 0  
 Basic O = 0  
 Mineral content is neither acidic nor basic  
 N and O are not amphoteric

Analysis of the recycle solvents of these SRC samples indicated that the concentration of carbazole and its methylated derivatives remained essentially constant, while the concentration of phenol and its methylated derivatives increased sixfold between SRC I and SRC II process conditions (6). These results are consistent with the hypothesis presented here.

#### REFERENCES

1. Appell, H.R. and I. Wender. Div. Fuel Chem. preprints. Amer. Chem. Soc. 12 (3) 220 (1968).
2. Knudson, C.L., J.E. Schiller, and A.L. Ruud. Div. Fuel Chem. preprints. Amer. Chem. Soc. 22 (6) 49 (1977).
3. Sondreal, E.A., C.L. Knudson, J.E. Schiller, and T.H. May. Proc. Ninth Biennial Lignite Symposium, Grand Forks, ND, May 1977.
4. Schiller, J.E., B.W. Farnum, and E.A. Sondreal. Div. Fuel Chem. preprints. Amer. Chem. Soc. 22 (6) 33 (1977).
5. Schiller, J.E. and D.R. Mathiason. Anal. Chem. 49, 1225 (1977).
6. Schiller, J.E. Hydrocarbon Processing 56, 147 (1977).



Table 1. Properties of Solubility Fractions of CO-Steam Products

CO-Steam Product	A		B		C	
	Wt. %	MW	Wt. %	MW	Wt. %	MW
Solubility fractions.....						
Oil (hexane soluble).....	55.9	403	48.7	385	52.3	281
Asphaltene (toluene soluble hexane insoluble).....	22.6	554	18.4	542	22.8	345
Preasphaltene (THF soluble toluene insoluble)....	20.9	747	17.9	611	4.7	501
Tetrahydrofuran insoluble.....	0.6	---	15.0	---	20.2	---
Process Temp. (°C).....	425		450		470	
Acidity (Meq H <sup>+</sup> /g):						
Oil.....	1.587		1.361		0.513	
Asphaltene.....	1.945		2.449		0.873	
Preasphaltene.....	1.974		2.052		1.058	
THF insoluble.....	1.518		1.027		0.266	
Total Product.....	1.729		1.725		0.544	
Calculated Acidity <sup>a</sup> .....	1.748		1.635		0.571	

<sup>a</sup> Acidity calculated as the weighted sum of the acidities of the individual fractions.

Table 2. Acid-Base Content of Column Chromatography Fractions

	CO-Steam A		CO-Steam B	
	Acidity (Meq/g)	Basicity (Meq/g)	Acidity (Meq/g)	Basicity (Meq/g)
1. Hydrocarbons.....	0	0	0	0
2. N Fraction.....	---	0.724	3.687	0.942
3. OH Fraction.....	2.98	0.217	2.806	0.216

Table 3. Acid-Base Properties of Non-Distillables





Sample	Acidity (Meq/g)	Pct O	Basicity (Meq/g)	Pct N	Pct N Basic	Pct N Acidic	Pct O Acidic	Pct O Neutral
SRC 115	1.481	1.55	0.711	1.70	0.995	0.718	1.55	0
CO-Steam Residue B	1.938	3.72	0.476	1.23	0.67	0.56	2.46	1.26
CO-Steam Residue A	1.661	7.03*	0.449	1.15	0.63	0.52	2.07	4.96*
SRC 308	2.285	4.32	0.786	1.78	1.10	0.68	2.88	1.44
SRC 122	2.531	4.69	0.713	1.55	1.00	0.55	3.42	1.27

\* Not deashed; illustrates mineral oxygen.

Figure 1.

- A. PERC Stirred Reactor  
B. PERC Tubular Reactor  
C. GFERC Batch Reactor

Solubility Fractions:

-  Hexane Soluble (oil)  
 Asphaltene (solid)  
 Preasphaltene (solid)  
 THF Insoluble (solid)

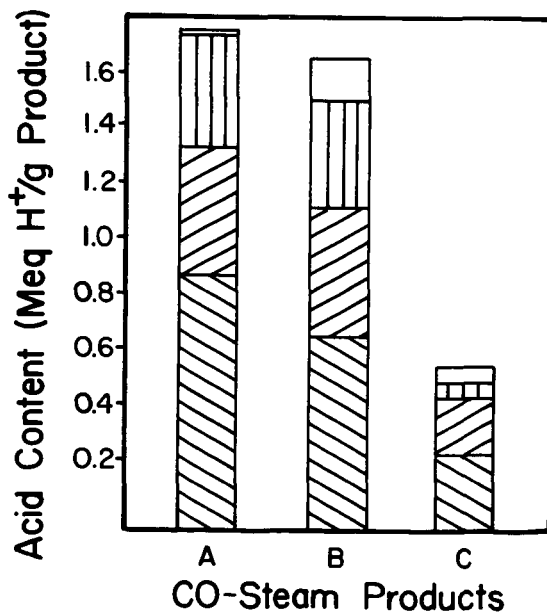


FIGURE 2

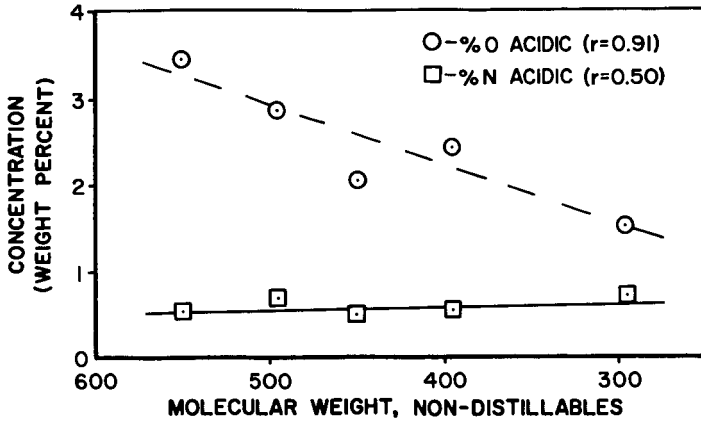
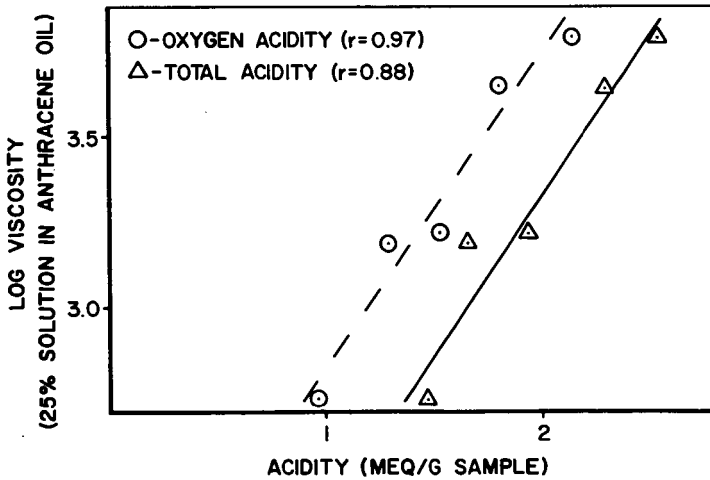


FIGURE 3



## LIQUID CHROMATOGRAPHIC CHEMICAL CLASS ANALYSIS OF BITUMEN AND HEAVY PETROLEUM CRUDES

C. Reichert and L. Grant  
Oil Sands Research Centre  
Alberta Research Council  
Edmonton, Alberta T6G 2C2

### INTRODUCTION

The importance of bitumen and heavy crudes is steadily increasing as reserves of conventional crudes diminish around the world producing an increased emphasis upon the development of methods of recovery for bitumens and heavy crudes. Because of the extremely high viscosities encountered, a variety of novel in-situ recovery methods using combinations of steam, solvents, surfactants, and combustion are being investigated.

Conventional and heavy petroleum crudes consist of a large variety of organic molecules generally classified into four major groups identified as saturates, aromatics, resins and asphaltenes. Each of these classes have individual uses and their relative ratios determine the upgrading processes employed. Bitumen and heavy crudes tend to have larger proportions of resins and asphaltenes that are less economically converted to usable products. Precipitation of asphaltenes in the formation or production of asphaltenes from other compounds can occur during the recovery process necessitating some monitoring of process streams for changes in the relative ratios of these classes of compounds.

Numerous methods are used to separate petroleum hydrocarbons into their type and classes. The most common method utilizes pentane precipitation of the asphaltenes in a procedure similar to ASTM D 893-69. A variety of procedures (1-6) are employed for the subsequent fractionation of the remaining oil. Many of the procedures for the separation of the aromatics and saturates using silica and/or alumina columns are modifications of ASTM D 2549-75. Some of the methods achieve separations into subgroupings such as monoaromatics, diaromatics, polyaromatics and polar compounds.

Each of the procedures however has the disadvantage that a total class analysis requires several steps and to obtain the data regarding the distribution of the fractions requires several days.

The procedure discussed here enables the separation of the bitumen or heavy petroleum crude into three groupings namely asphaltenes, resins and a mixture of aromatics and saturates with no prior separation of the polar constituents or of backflushing of the columns. Using a 254 nm UV detector it is possible to quantify each of the fractions in the bitumen.

### EXPERIMENTAL

The liquid chromatograph used in this study was a Varian Model 8500 dual syringe pump instrument equipped with a Varian Aerograph 254 nm UV detector connected to a Varian CDS 111 Data System. The columns used were a 25 cm Varian Aerograph Micropak CH-10 connected in series with a 25 cm Varian Aerograph Micropak CN-10.

Two mobile phase systems can be used to achieve the separation. One system employed 99% methanol-1% isopropanol for 4 minutes, 40% of the 99% methanol-1% isopropanol mixture-60% tetrahydrofuran for 10 minutes and finally 100% THF for 10 minutes. The second system used 90% acetonitrile-10% water for 5 minutes followed by 50% acetonitrile mixture-50% methylene chloride for 10 minutes followed finally by 100% methylene chloride for 10 minutes. Separation achieved by the two methods is comparable and is accomplished in 25-30 minutes using a flow rate of 60 cc/hr.

The bitumen/heavy crude samples are dissolved in methylene chloride at a concentration of 10-20 mg/ml with 2-5  $\mu$ l of sample being injected on the columns.

#### DISCUSSION AND RESULTS

Figure 1 shows a typical chromatogram of the separation of saturates and aromatics, resins, and asphaltenes in samples of Athabasca Bitumen. Superimposed on the chromatogram is a plot of the change in the solvent gradient during the analysis.

Chromatograms of aromatics and resins material obtained by separation on passage through attapulugus clay and silica-alumina columns successively are given in Figures 2 and 3 respectively. The chromatograms show that the aromatics produced by column chromatography contain material that we classified as resins by this procedure while the resin samples contain some aromatic material and also some asphaltene material. A chromatogram of an asphaltene sample obtained by pentane precipitation is given in Figure 4 which shows the presence of a resins peak. It is evident from these chromatograms that a very similar fractionation of the bitumen is obtained in our HPLC method as compared to the conventional column separation. Saturates material in the bitumen is eluted with the aromatics fraction however since saturates absorption at 254 nm is negligible they are not detected. By evaluation of the amount of aromatics, resins and asphaltenes the percentage of each of the four fractions in a bitumen sample can be determined.

#### CONCLUSIONS

The HPLC method discussed in this paper achieves a separation of bitumen into its class components i.e., asphaltenes, resins and mixture of aromatics and saturates, in proportions comparable to that obtained in classical separation by asphaltene precipitation with pentane and subsequent successive passage through attapulugus clay and silica alumina columns.

#### ACKNOWLEDGMENT

This study was funded by the Alberta Oil Sands Technology and Research Authority.

#### LITERATURE CITED

- (1) G.L. Brown and A.L. Jones, Hydrocarbon Processing Petrol Refiner, 39, 156 (1960).
- (2) J. Coleman, J.E. Dooley, D.E. Hirsch and C.J. Thompson, Analytical Chemistry, 45, 1724 (1973).

- (3) H. Sawtzky, A.E. George, G.T. Smiley and D.S. Montgomery, Fuel, 54, 16 (1976).
- (4) G.N. Pozdnyshev, R.I. Masurov and R.M. Ruchkina, Chemical Technology of Fuel and Oils, 10, 806 (1974).
- (5) J.C. Suatoni and H.R. Garber, J. Chromatog, Science, 14, 546 (1976).
- (6) U.S. Bureau of Mines, API-RP-60 (1974).

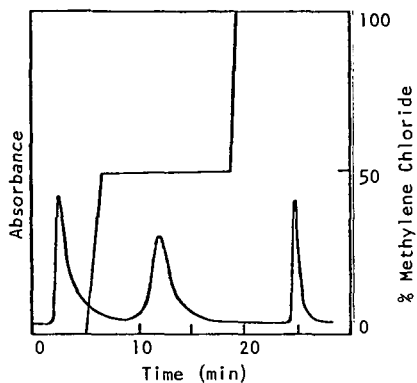


FIGURE 1 Chromatogram of Toluene Extracted Bitumen

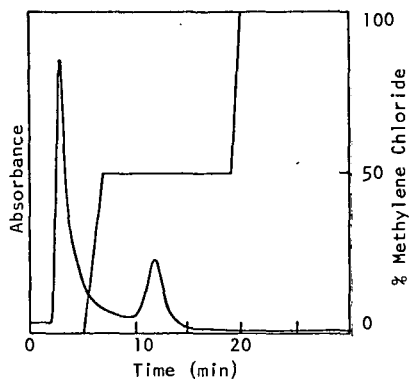


FIGURE 2 Chromatogram of an Aromatics Fraction Separated on Silica-Alumina

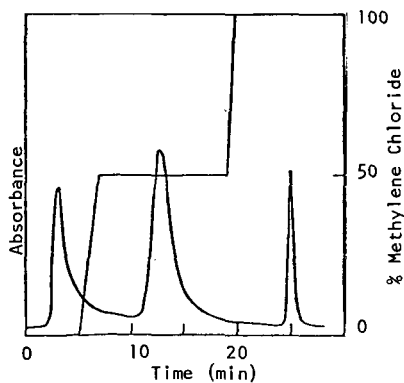


FIGURE 3 Chromatogram of a Resins Fraction Separated on Attapulugus Clay

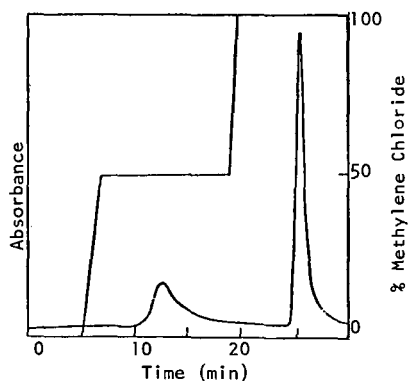


FIGURE 4 Chromatogram of an Asphaltene Fraction Precipitated by Pentane

COMPARISON OF METHODS FOR DETERMINING ASPHALTENES IN  
COAL-DERIVED LIQUID FUELS

H. Schultz and M. J. Mima

DEPARTMENT OF ENERGY  
PITTSBURGH ENERGY RESEARCH CENTER  
4800 Forbes Avenue  
Pittsburgh, Pennsylvania 15213

There is at present no standard method for the determination of asphaltenes in the products of coal conversion, nor is there any known relationship between the values for asphaltene concentration produced by the various analytical methods currently in use. Lacking a standard method of analysis, are comparisons of the coal conversion products of the various processes possible? The research described in this paper attempts to answer this question at least in part.

Five different solvent separation methods which are currently in use for determining asphaltenes in coal-derived liquids have been studied in the analytical chemistry laboratory of the Pittsburgh Energy Research Center of the U. S. Department of Energy. The material chosen for the tests was a liquid product which was produced from the Center's 0.5 ton-per-day hydrodesulfurization plant. The material was produced using a fixed-bed cobalt-molybdenum catalyst, 4,000 psi hydrogen, and a temperature of 450 °C. The Homestead, Kentucky coal was slurried in coal-derived oil (35% by weight coal) and fed to the plant at 25 pounds per hour. A single sample of the liquid product was taken, separated into five portions, and stored in the refrigerator under nitrogen.

Twenty replicate determinations of asphaltenes were made with each test method, relying not only on written procedures but also on personal contacts with the authors of each method. Data collected include weight percent asphaltenes, insolubles, and oils. Standard deviations were calculated for each method and statistical comparisons made between methods.

The following are short descriptions of the five procedures studied:

Method A: A ten-gram sample is extracted with benzene in a Soxhlet apparatus. The benzene is removed on a steam bath, and 5 ml. of benzene are added to the residue. Asphaltenes are precipitated with 250 ml of n-pentane, and separated by filtration through the paper.

Method B: A three-gram sample is frozen and pulverized in liquid nitrogen and n-pentane is added. The sample is mixed and crushed while in an ultrasonic bath, and then centrifuged. The supernatant liquid is decanted into a rotary evaporator flask and the pentane washing procedure and centrifugation repeated three times. The combined supernatant solutions are then evaporated with nitrogen to recover the oil. Benzene is added to the insoluble material in the centrifuge tubes and the mixing, sonication, and centrifugation are carried out in the same manner as with the n-pentane. The supernatant benzene solutions are combined, evaporated under nitrogen, and finally freeze-dried to obtain the asphaltenes.

Method C: A three-gram sample is extracted under nitrogen with toluene in a Soxhlet apparatus. The toluene is removed from the extract in a rotary evaporator using a water aspirator. Exactly two ml of toluene per gram of soluble material are added



and the asphaltenes are precipitated with a volume of n-pentane equal to twenty times the volume of toluene that was added. The precipitate is then extracted with n-pentane in a Soxhlet apparatus.

Method D: Ten grams of sample are mixed with benzene, stirred for 30-60 minutes at 30 °C, and centrifuged. The benzene solution is decanted and the residue is washed with fresh benzene four times. The solvent is stripped from the combined supernatant liquid in vacuo at 30 °C, and finally the material is freeze-dried. The residue is dissolved in five ml. of benzene and the asphaltenes are precipitated with a liter of hexane. The solids are separated by centrifugation, the supernatant is stripped of hexane, and the precipitation procedure is repeated. The supernatants are combined and stripped as before, and the asphaltenes are freeze-dried.

Method E: A 25-gram sample is refluxed with benzene. The supernatant liquid is centrifuged and then filtered through paper under cover of nitrogen. The residue in the centrifuge tubes is refluxed with benzene, centrifuged, and filtered three more times. The collected extracts are evaporated under vacuum in a rotary evaporator at 105 °F. Cyclohexane is added to precipitate the asphaltenes and the mixture is refluxed under nitrogen. Centrifugation and filtration are carried out as above and are repeated once or twice depending on the color of the supernatant liquid. The reflux flask, centrifuge bottles, and filter paper are dried in vacuo and weighed to obtain the weight of the asphaltenes.

Table 1 shows the results obtained with the first three methods described above:

Table 1. - Results with Methods A, B, and C

	<u>% Insolubles <math>\pm 1s</math></u>	<u>% Asphaltenes <math>\pm 1s</math></u>	<u>% Oils <math>\pm 1s</math></u>
Method A	5.2 $\pm 0.3$	26.9 $\pm 0.7$	67.9 $\pm 0.7$ (by difference)
Method B	7.6 $\pm 0.5$	23.8 $\pm 0.7$	67.2 $\pm 0.9$
Method C	4.6 $\pm 0.5$	22 $\pm 2$	70 $\pm 3$

The data indicate that the relative standard deviations for asphaltenes range from 2.6 to 6.8%, well within the range of acceptability for a separation procedure for coal-derived materials. There was considerable variation between methods in the length of time necessary to complete an analysis, in the amount of time expended by the analyst, and in the production rate.

In order to determine if the analytical results produced by each of the methods were significantly different, Student's 't' test was applied to the average of the 20 replicate analyses. Table 2 shows the findings obtained with the first three methods.

Table 2. - Significance\* of Differences Between Methods

<u>Methods Compared</u>	<u>Insolubles</u>	<u>Asphaltenes</u>	<u>Oils</u>
A vs. B	Significant	Significant	Not significant
A vs. C	Significant	Significant	Not significant
B vs. C	Significant	Not significant	Not significant

\*Student's 't' test - at the 95% confidence level.

It is evident that in half the comparisons made the difference proved to be significant. From the results obtained in this study one can surmise that the conclusions drawn from the comparison of the analyses of coal-derived liquids produced by different analytical procedures are problematical at best. One can also conclude that some acceptable "standard" method for the determination of asphaltenes in coal-derived liquids is urgently needed.